CERTIFICATION OF TRANSLATION

I, Hiroshi Takayama, residing at 6th Floor, Shin-Yokohama IC Building, 18-9, Shin-Yokohama 3-chome, Kohoku-ku, Yokohama-shi, Kanagawa Japan, state:

that I know well both the Japanese and English languages;

that I translated, from Japanese into English, the specification and claims as filed in U.S. Patent Application No. 60/423,566, filed November 5, 2002; and

that the attached English translation is a true and accurate translation to the best of my knowledge and belief.

December 12, 2003
Date

Hiroshi Takayama
Translator Hiroshi Takayama

Specification

[Title of the Invention]

Method of Processing Process Subject

[Field of the Invention]

The present invention relates to a process performed in the process of manufacturing semiconductor devices, and particularly to a process of improving the plasma resistance of a mask layer and a process of plasma etching.

[Conventional Art]

When plasma etching is performed on an etching objective layer, a resist mask formed of, e.g., a photoresist is used. Particularly, in accordance with demands for micro-patterning, a photoresist frequently used in recent years is an ArF photoresist or F2 photoresist, i.e., a photoresist to be exposed to laser light from a light source of ArF gas or F_2 gas, which is suitable for forming an opening pattern of about 0.13 m or less.

However, since the ArF photoresist layer and F2 photoresist layer have a low plasma resistance, they cause a problem in that the surface of the photoresist layer becomes rough during etching. If the surface of the photoresist layer becomes rough, the shapes of

opening portions are deformed with the etching progress, thereby making it difficult to obtain the designed shapes of etched holes or etched grooves. Furthermore, during etching, the photoresist disappears at some positions, and the etching proceeds to portions that are designed to be non-etched.

As a method of improving the plasma resistance of a photoresist layer, there is a method of irradiating the surface of a photoresist layer with ultraviolet rays, an electron beam, or an ion beam, a method of heat-setting a photoresist, or a method of applying heat or light energy to an organic silicon compound to coat the surface of a photoresist layer with a thin cured layer.

In the above-described methods of improving the plasma resistance of a photoresist layer, it is necessary to perform a process of improving the plasma resistance in a container other than a container used in an etching step performed thereafter. Since a process subject to be processed needs to be transferred from the container for performing the process of improving the plasma resistance of a photoresist layer to the etching container, the yield is lowered in the transfer step and throughput is lowered due to a necessary transfer time. Furthermore, since the container for performing the process of improving the plasma resistance needs to be provided independently of

the etching container, not only an additional space is required, but also the cost increases.

The etching container may be provided additionally with ultraviolet ray radiating means or heating means without independently disposing a container for performing the process of improving the plasma resistance. In this case, however, since the structure still requires the ultraviolet ray radiating means or heating means, the cost also increases.

[Disclosure of Invention]

In order to solve the problems described above, a first invention is directed to a method of processing a process subject, comprising the steps of: placing a process subject in a process container, wherein the process subject has an etching objective layer, and a mask layer covering the etching objective layer and having an opening formed therein; supplying a process gas containing H_2 into the process container, and turning the process gas into plasma; and irradiating the mask layer with the plasma in an atmosphere having a pressure of 100 mTorr or less. When the mask layer is irradiated with plasma of a process gas containing H_2 in an atmosphere having a low pressure of 100 mTorr or less, its surface is reformed, thereby improving the plasma resistance of the mask layer. Since the plasma resistance of the mask layer is improved, the

selectivity of the etching objective layer relative to the mask layer, i.e., the etching rate of the etching objective layer / the etching rate of the mask layer, becomes high, in a step performed thereafter of plasma-etching the etching objective layer through an opening of the mask layer. Furthermore, in this etching step, the mask layer is prevented from suffering stripe or groove formation thereon due to plasma. Furthermore, it is possible to prevent the opening portion from being expanded in the mask layer. Although it is not clear in detail, the mechanism for improving the plasma resistance of the mask layer seems to be as follows. Specifically, H radicals act on the surface layer of the mask layer to remove a gas of CH_4 or the like from the mask layer, thereby modifying the chemical bonds between carbons in the mask layer to be stronger.

A second invention is directed to a method of processing a process subject, comprising the steps of: placing a process subject in a process container, wherein the process subject has an etching objective layer, an antireflective layer covering the etching objective layer, and a mask layer covering the antireflective layer and having an opening formed therein; supplying a process gas containing H_2 into the process container, and turning the process gas into plasma; and irradiating the mask layer with the plasma in an atmosphere having a pressure of 100 mTorr or less.

Even where the antireflective layer of the process subject is exposed, the plasma resistance of the mask layer can be improved. The antireflective layer is used to prevent deviation in shape of a portion to be etched of the etching objective layer, and in shape of the opening portion of the mask layer covering the etching objective portion. For this reason, the antireflective layer is interposed between the etching objective portion and mask layer. The antireflective layer is made of an inorganic material, such as a metal, or metal compound, e.g., a metal nitride, an organic material containing carbon as the main component or a hybrid organic-inorganic material. This matter is common to the inventions described above and inventions described below.

A third invention is directed to a method of processing a process subject, comprising the steps of: placing a process subject on a susceptor disposed in a process container, wherein the process subject has an etching objective layer, and a mask layer covering the etching objective layer and having an opening formed therein; supplying a process gas containing H_2 into the process container; supplying the susceptor with a high-frequency power having a frequency of 100 MHz or more; and setting a pressure in the process container at 100 mTorr or less. Also in a plasma processing apparatus that is provided with the susceptor to be supplied with

a high-frequency power having a frequency preferably of 100 MHz or more, the plasma resistance of the mask layer can be improved. In this case, where the susceptor is supplied with another high-frequency power having a frequency preferably of 3 MHz or more, it is possible to control active species, particularly ions, in plasma. This other high-frequency power is set preferably at 100W or less. Where the process is performed under an atmosphere of a low pressure and low power (low bias), the mask layer can be damaged at the minimum. Furthermore, under an atmosphere of a low pressure and low power (low bias), H radicals penetrate into the inside from the sidewall of the mask layer, so that the plasma resistance is improved over a large thickness from the sidewall surface to the inside of the mask layer. Since the mask layer is made preferably of a material containing carbon, and particularly an organic substance. This is so, because the surface reformation effect is remarkable on a mask layer of an organic substance. Furthermore, of the organic mask layers, an ArF photoresist mask or F2 photoresist mask changes its plasma resistance to a considerable extent between before and after the plasma resistance improvement process. Accordingly, the process described above has a profound effect if it is applied to a step of micro-patterning for it. The ArF photoresist or F2 photoresist may be made of an

alicyclic group-containing acrylate resin, cycloolefin resin, cycloolefin-maleic anhydride resin, or the like.

A fourth invention is directed to a method of processing a process subject, comprising the steps of: placing a process subject in a process container, wherein the process subject has an etching objective layer, an antireflective layer covering the etching objective layer, and a mask layer covering the antireflective layer and having an opening formed therein; supplying a process gas containing H_2 into the process container, and turning the process gas into plasma; and irradiating the process subject with the plasma, thereby improving plasma resistance of the mask layer while etching the antireflective layer at the same time. According to this method, when the etching of the antireflective layer necessary for etching of the etching objective layer is performed, not only the mask layer is almost prevented from being etched, but also the plasma resistance of the mask layer is improved.

A fifth invention is directed to a method of processing a process subject, comprising the steps of: placing a process subject on a susceptor disposed in a process container, wherein the process subject has an etching objective layer, an antireflective layer covering the etching objective layer, and a mask layer covering the antireflective layer and having an opening

formed therein; supplying a process gas containing H_2 into the process container; and supplying the susceptor with a high-frequency power having a frequency of 100 MHz or more, thereby improving plasma resistance of the mask layer while etching the antireflective layer at the same time. When the susceptor is supplied with a high-frequency power having a frequency of 100 MHz or more, H_2 is dissociated in the process container and forms various active species. Of the active species, H radicals mainly contribute to improvement in the plasma resistance of the mask layer, while H radicals and ions contribute to etching of the antireflective layer. Since the active species have a good contribution balance, it is possible to improve the plasma resistance of the mask layer, while effectively etching the antireflective layer at the same time. Furthermore, where the susceptor is supplied with another high-frequency power from a high-frequency power supply having a frequency of 3 MHz or more, movement of ions in the active species can be controlled. At this time, the high-frequency power having a frequency of 3 MHz or more is set at 100W or less, so that the plasma resistance is improved over a large thickness from the sidewall surface to the inside of the mask layer. As a result, it is possible to prevent reduction of the mask layer, stripe or groove formation on the mask layer, and expansion of the opening area of the mask layer, in

the following step of plasma-etching the etching objective layer.

A sixth invention is directed to a method of processing a process subject, comprising the steps of: placing a process subject in a process container, wherein the process subject has an etching objective layer, an antireflective layer covering the etching objective layer, and a mask layer covering the antireflective layer and having an opening formed therein; supplying a process gas containing H_2 into the process container, and turning the process gas into plasma; and selectively plasma-etching the antireflective layer relative to the mask layer through the opening of the mask layer. According to this method, H_2 supplied into the process container is turned into plasma, and etches the antireflective layer while hardly etching the mask layer. In other words, it is possible to selectively etch the antireflective layer relative to the mask layer.

A seventh invention is directed to a method of processing a process subject, comprising the steps of: placing a process subject on a susceptor disposed in a process container, wherein the process subject has an etching objective layer, an antireflective layer covering the etching objective layer, and a mask layer covering the antireflective layer and having an opening formed therein; supplying a process gas containing H_2

into the process container; and supplying the susceptor with a high-frequency power having a frequency of 100 MHz or more, thereby selectively plasma-etching the antireflective layer relative to the mask layer through the opening of the mask layer. According to this method, it is possible to selectively etch the antireflective layer relative to the mask layer. The susceptor may be supplied with a high-frequency power having a frequency of 3 MHz or more, other than the high-frequency power. In this case, the other high-frequency power is set preferably at 100W or less.

In any of these inventions, where the mask layer is an ArF photoresist layer or F2 photoresist layer, the effect becomes remarkable. This is so, because the ArF photoresist layer or F2 photoresist layer has a low plasma resistance. As a matter of course, the present invention is also effective in a mask layer having a low plasma resistance, other that the ArF photoresist layer or F2 photoresist layer. The effect of the present invention can be obtained, even where the process gas consists only of H_2, or further contains a dilution gas, such as Ar, at a flow rate almost the same as that of H_2. The process gas preferably contains no substance having N, because of the following reason. If the process gas contains a substance having N, the sidewall surface of the mask layer is covered with a protection film containing C and N as the main

component. The protection film prevents H radicals, which are likely to act for the plasma resistance improvement, from penetrating into the inside from the sidewall surface. As a consequence, it is difficult to improve the plasma resistance of the sidewall surface of the mask layer over a large thickness. Furthermore, the process pressure is set preferably at 8 to 30 mTorr to reduce damages to the mask layer in the process.

[Embodiments of the Invention]

FIG. 1 is a sectional view showing a processing apparatus 1, which can perform the present invention. There is a process container 2, which is made of a metal, such as aluminum with an anodized surface, and is grounded. The process container 2 is provided with a susceptor 5 disposed therein on the bottom through an insulator 3. The susceptor 5 is made of a conductive material, such as aluminum with an anodized surface, and functions as the lower electrode of parallel-plate electrodes. An electrostatic chuck 11 is provided on the susceptor 5 to place a process subject W, such as a semiconductor wafer, thereon. The process subject W has an etching objective layer of a silicon oxide layer or the like, an antireflective layer covering the etching objective layer, and a mask layer of an ArF photoresist layer, F2 photoresist layer, or the like, covering the antireflective layer, and having an

opening formed therein. The etching objective layer is not limited to the silicon oxide layer. The present invention may be applied to oxide film (oxygen compound) such as TEOS, BPSG, PSG, SOG, thermal oxidation film, HTO, FSG, organic silicon oxide film, CORAL (Novellus Systems), low dielectric constant organic insulating film, metal, metal compound, or the like.

The electrostatic chuck 11 is arranged such that an electrode 12 is sandwiched between insulators. The electrode 12 is supplied with a DC voltage from a DC power supply 13 connected thereto, so that the process subject W is attracted and held by means of electrostatic force. A focus ring 15 made of silicon, SiO_2, or the like is disposed around the process subject W to improve etching uniformity.

An upper electrode plate 21, which is made of silicon or the like, and has a structure as a showerhead, is supported by an upper portion of the process container 2 above the susceptor 5 to face the susceptor 5. The process container 2 also functions as an electrode of the parallel-plate electrodes to face the susceptor.

A gas inlet port 26 is formed at the center of the top of the process container 2. The gas inlet port 26 is connected to a gas supply line 27, valve 28, mass-flow controller 29, and process gas supply source 30 in

this order. The process gas supply source 30 can supply H_2, He, Ar, and the like, C_4F_6, C_4F_8, C_5F_8, and the like, and O_2, N_2, CO, and the like.

On the other hand, the bottom of the process container 2 is connected to an exhaust line 31, which is connected to an exhaust device 35. The process container 2 is provided with a gate valve 32 on the sidewall, so that the process subject W can be transferred between the process container 2 and an adjacent load-lock chamber (not shown).

The susceptor 5 functioning as the lower electrode is connected to a first high-frequency power supply 40 and a second high-frequency power supply 50 through matching devices 41 and 51, respectively. The first and second high-frequency power supplies 40 and 50 have frequencies of, e.g., 100 MHz and 3.2 MHz, respectively. The structure of the processing apparatus is not limited to that shown in FIG. 1.

Next, an explanation will be give of the procedure for processing the process subject W.

The gate valve 32 is first opened, and the process subject W is transferred into the process container 2 and placed on the electrostatic chuck 11. Then, the gate valve 32 is closed, and the pressure in the process container 2 is reduced by the exhaust device 35. Then, the valve 28 is opened, and a process gas, such as H_2, is supplied from the process gas supply source 30,

thereby setting the pressure in the process container 2 at a predetermined value. In this embodiment, the pressure in the chamber was set at three values of 1.07 Pa (8.0 mTorr), 4.00 Pa (30 mTorr), and 13.3 Pa (100 mTorr). In this state, high-frequency powers are applied from the first and second high-frequency power supplies 40 and 50 to turn the process gas into plasma to act on the process subject W.

Before or after the timing when the high-frequency powers are applied, a DC voltage is applied to the electrode 12 in the electrostatic chuck 11 from the DC power supply 13 to electrostatically attract and hold the process subject W on the electrostatic chuck 11. The first and second high-frequency power supplies connected to the susceptor 5 were set to supply powers of 2,400W and 500W, respectively. Evaluation was also performed in a case where no power was supplied from the second high-frequency power supply (= 0W). The evaluation was performed by observing the sectional state of the mask layer with a microscope (SEM).

As a result, when the pressure was set at 1.07 Pa (8.0 mTorr), or 4.00 Pa (30 mTorr), stripe or groove formation on the mask layer and expansion of the opening portion hardly occurred. When the pressure was set at 13.3 Pa (100 mTorr), stripe or groove formation on the mask layer and expansion of the opening portion occurred a little. As the pressure was higher, stripe

or groove formation on the mask layer occurred more easily. As the pressure was higher, stripe or groove formation on the mask layer occurred more easily.

As regards the power supplied from the second high-frequency power supply, stripe or groove formation on the mask layer and expansion of the opening portion were less at 0W than at 500W. In light of these results, the power supplied from the second high-frequency power supply is set preferably at 100W or less.

Furthermore, the flow rate of the process gas of H_2 was changed and set at 50 sccm, 100 sccm, 120 sccm, and 200 sccm, while the pressure was fixed at 1.07 Pa (8.0 mTorr). As a consequence, as the flow rate was lower, stripe or groove formation on the mask layer and expansion of the opening portion were less.

In the step performed thereafter of etching the etching objective layer, an etching gas is supplied into the process container. For example, where the etching objective layer is a silicon oxide layer, the etching gas is a mixture gas of C_4F_6, O_2, and Ar. The pressure in the process container is set at 6.66 Pa (50 mTorr). The susceptor 5 was supplied with high-frequency powers, at 600W from the first high-frequency power supply, and at 1,800W from the second high-frequency power supply. The first high-frequency power is supplied to turn the etching gas into plasma,

thereby etching the silicon oxide layer disposed as an etching objective layer. The etching is finished on the basis of an end-point detection method or the like. Even after the plasma etching of the etching objective layer, large reduction of the mask layer, stripe or groove formation on the mask layer, and expansion of the opening portion of the mask layer were hardly observed. Accordingly, it was confirmed that the improvement effect on the plasma resistance of the mask layer according to the present invention remained even after the plasma etching of the etching objective layer.

[Claims]

1. A method of processing a process subject, comprising the steps of:

placing a process subject in a process container, wherein the process subject has an etching objective layer, and a mask layer covering the etching objective layer and having an opening formed therein;

supplying a process gas containing H_2 into the process container, and turning the process gas into plasma; and

irradiating the mask layer with the plasma in an atmosphere having a pressure of 100 mTorr or less.

2. The method of processing a process subject according to claim 1, further comprising a step of plasma-etching the etching objective layer through the opening of the mask layer, after the step of irradiating the mask layer with the plasma in an atmosphere having a pressure of 100 mTorr or less.

3. A method of processing a process subject, comprising the steps of:

placing a process subject in a process container, wherein the process subject has an etching objective layer, an antireflective layer covering the etching objective layer, and a mask layer covering the antireflective layer and having an opening formed therein;

supplying a process gas containing H_2 into the

process container, and turning the process gas into plasma; and

irradiating the mask layer with the plasma in an atmosphere having a pressure of 100 mTorr or less.

4. A method of processing a process subject, comprising the steps of:

placing a process subject on a susceptor disposed in a process container, wherein the process subject has an etching objective layer, and a mask layer covering the etching objective layer and having an opening formed therein;

supplying a process gas containing H_2 into the process container;

supplying the susceptor with a high-frequency power having a frequency of 100 MHz or more; and

setting a pressure in the process container at 100 mTorr or less.

5. The method of processing a process subject according to claim 4, further comprising a step of supplying the susceptor with a high-frequency power having a frequency of 3 MHz or more, other than the high-frequency power.

6. The method of processing a process subject according to claim 5, wherein the high-frequency power having a frequency of 3 MHz or more is set at 100W or less.

7. A method of processing a process subject,

comprising the steps of:

placing a process subject in a process container, wherein the process subject has an etching objective layer, an antireflective layer covering the etching objective layer, and a mask layer covering the antireflective layer and having an opening formed therein;

supplying a process gas containing H_2 into the process container, and turning the process gas into plasma; and

irradiating the process subject with the plasma, thereby improving plasma resistance of the mask layer while etching the antireflective layer at the same time.

8. A method of processing a process subject, comprising the steps of:

placing a process subject on a susceptor disposed in a process container, wherein the process subject has an etching objective layer, an antireflective layer covering the etching objective layer, and a mask layer covering the antireflective layer and having an opening formed therein;

supplying a process gas containing H_2 into the process container; and

supplying the susceptor with a high-frequency power having a frequency of 100 MHz or more, thereby improving plasma resistance of the mask layer while etching the antireflective layer at the same time.

9. The method of processing a process subject according to claim 8, further comprising a step of supplying the susceptor with a high-frequency power having a frequency of 3 MHz or more, other than the high-frequency power.

10. The method of processing a process subject according to claim 9, wherein the high-frequency power having a frequency of 3 MHz or more is set at 100W or less.

11. The method of processing a process subject according to any one of claims 7 to 10, further comprising a step of plasma-etching the etching objective layer through the opening of the mask layer, after the step of improving plasma resistance of the mask layer while etching the antireflective layer at the same time.

12. A method of processing a process subject, comprising the steps of:

placing a process subject in a process container, wherein the process subject has an etching objective layer, an antireflective layer covering the etching objective layer, and a mask layer covering the antireflective layer and having an opening formed therein;

supplying a process gas containing H_2 into the process container, and turning the process gas into plasma; and

selectively plasma-etching the antireflective layer relative to the mask layer through the opening of the mask layer.

13. A method of processing a process subject, comprising the steps of:

placing a process subject on a susceptor disposed in a process container, wherein the process subject has an etching objective layer, an antireflective layer covering the etching objective layer, and a mask layer covering the antireflective layer and having an opening formed therein;

supplying a process gas containing H_2 into the process container; and

supplying the susceptor with a high-frequency power having a frequency of 100 MHz or more, thereby selectively plasma-etching the antireflective layer relative to the mask layer through the opening of the mask layer.

14. The method of processing a process subject according to claim 13, further comprising a step of supplying the susceptor with a high-frequency power having a frequency of 3 MHz or more, other than the high-frequency power.

15. The method of processing a process subject according to claim 14, wherein the high-frequency power having a frequency of 3 MHz or more is set at 100W or less.

16. The method of processing a process subject according to any one of claims 1 to 15, wherein the mask layer is an ArF photoresist layer.

17. The method of processing a process subject according to any one of claims 1 to 15, wherein the mask layer is an F2 photoresist layer.

18. The method of processing a process subject according to any one of claims 1 to 17, wherein the process gas is H_2.

19. The method of processing a process subject according to any one of claims 1 to 17, wherein the process gas contains no substance having N.

20. The method of processing a process subject according to any one of claims 1 to 6, wherein the pressure is set at 8 to 30 mTorr.

(Drawing)

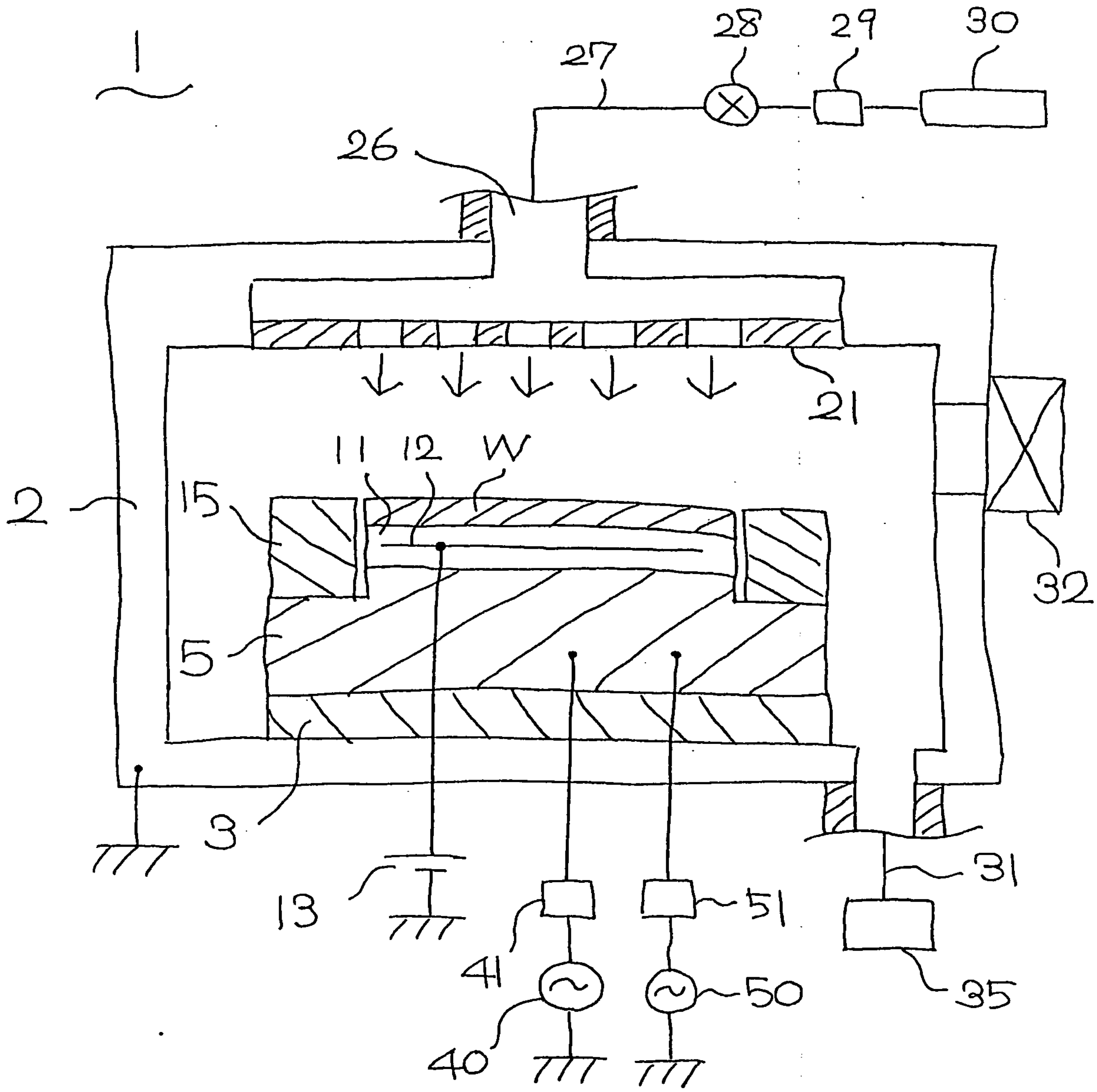

Fig. 1